JUNIPENONOIC ACID, A NOVEL $C_{9,10}$-SECOCADINANE SESQUITERPENE, FROM THE HEARTWOOD OF *JUNIPERUS FORMOSANA* HAY. VAR. *CONCOLOR* HAY.

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Junipenonoic acid (**4**), a novel $C_{9,10}$-secocadinane sesquiterpene, was isolated from the heartwood of *Juniperus formosana* HAY. var. *concolor* HAY. The structure was elucidated on the basis of spectral evidence. The absolute configuration was proposed as *S*.

KEY WORDS *Juniperus formosana* var. *concolor*; $C_{9,10}$-secocadinane sesquiterpene; junipenonoic acid

The components of *Juniperus* species (Cupressaceae) contain many kinds of skeleton.[1] The chemical principles of the heartwood of *J. squamata* LAMB var. *morrisonicola* HAY,[2] heartwood of *J. formosana* HAY,[3] root of *J. chinensis* LINN,[4] bark of *J. chinensis* LINN, var. *kaizuca* HORT *ex* ENDL,[5] heartwood of *J. chinesis* LINN var. *tsukusiensis* Masam,[6] and bark of *J. formosana* HAY var. *concolor* HAY[7] were studied in our laboratory. Recently, we have examined the chemical components of the methanolic extract of the the heartwood of the last species [three new ferruginol derivatives[8a] and two new sesquiterpenes, (-)-(7*S*, 10*S*)-15-hydroxycalamenene (**1**) and (-)-(7*S*)-1-hydroxy-1,3,5-bisabolatrien-10-one (**2**), together with two known sesquiterpenes, (-)-3-hydroxycalamenene and (-)-(*S*)-sesquichamaenol (**3**)].[8b] From the same extract, we have isolated a novel $C_{9,10}$-secocadinane sesquiterpene, junipenonoic acid (**4**). In this paper, we describe the structure elucidation and absolute configuration of this novel compound.

Junipenonoic acid (**4**), an amorphous solid, $[\alpha]_D$=-3.5 (*c* = 0.5, $CHCl_3$) was formulated as $C_{15}H_{20}O_3$ on the basis of (HR)-EIMS (M^+ *m/z* 248.1417, *calc.* 248.1413). It showed IR absorption bands at 3300-2500, 1707, 922 cm^{-1} (-COOH), 1685 (conjugated carbonyl), 1608, 1560, 1518 (aromatic absorption), and 1386, 1374 cm^{-1} (germinal dimethyl absorption) and UV absorption bands at λ_{max} (MeOH) 248 nm (ε=13120).

The ^{1}H-NMR spectrum (Table 1) revealed that **4** has an isopropyl group (δ 0.69, 0.96 [each 3H, d, *J*=6.6 Hz] and 1.79 [1H, m]), one methyl and one acetyl group attached to a phenyl group (δ 2.34 and 2.55 [3H each, s]), two methylene protons with ABX system signals vicinal to carboxylic acid (δ 2.62 [dd, *J*=16.5, 10.9 Hz], 2.88 [dd, *J*=16.5, 5.1 Hz]), a multiple benzylic methine proton (δ 3.43, m) and three 1,2,4-trisubstituted phenyl protons (δ7.09 [br.s], 7.05 [br d, *J*=8.3 Hz], 7.43 [d, *J*=8.3Hz]). On irradiation at δ 3.43, the signal at 1.79 collapsed into a septet (*J*=6.6 Hz) and the signals at 2.62 and 2.88 collapsed into doublets (*J*=16.5 Hz). NOESY crosspeaks, H-15/H-5, H-15/H-3, H-14/H-2, H-11/H-5,and H-8/H-5, support the notion that the acetyl group is *para* to the methyl group and *ortho* to the isohexanoic acid moiety. Isohexanoic acid with C-3 linked to the phenyl group was discernible using the spectral data decoupling technique. The structure of junepenonoic acid (**4**) can be assigned as 2-(1-isopropylpropanoic acid)-4-methylacetophenone. The structure is also confirmed

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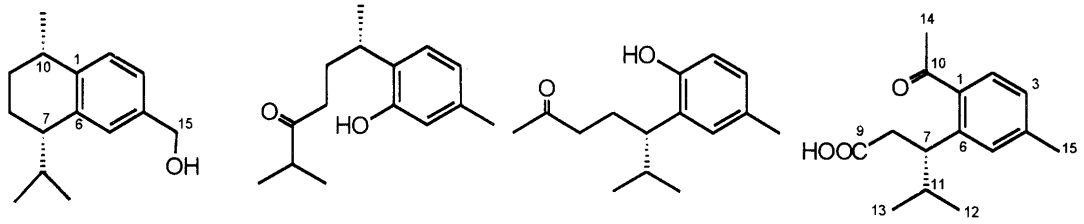
by HMQC and HMBC spectra (Table 1). It is a novel secocadinane and is considered to derive from α-calacorene by biological cleavage between C_9 and C_{10}. Compounds **4** and **3** also exhibited negative specific rotation, while the chiral centers of compounds **1**, **2**, and **3** were determined as *S*-configuration.[8b] Based on the same biological pathway and same negative specific rotation, compound **4** can therefore be deduced as the *S*-configuration. The biosynthesis of this plant is very interesting. It gave three kinds of secocadinane products; cleavage between C-1 and C-10 would give **3**, that between C-6 and C-7 would yield **2**, and that between C-9 and C-10 would afford **4**.



1 **2** **3** **4**

Table 1. NMR Data for Compound **4** (300 MHz, 75 MHz in $CDCl_3$)

No	δ_H	δ_C	HMBC correlation	No	δ_H	δ_C	HMBC correlation
1		141.9	H-2	9		175.0	H-8
2	7.43	128.3	H-3	10		204.5	H-2, H-14
3	7.05	126.8	H-5, H-15	11	1.79	33.8	H-12, H-13
4		137.1	H-3, H-5, H-15	12	0.69	21.0	H-13
5	7.09	128.2	H-15	13	0.96	20.2	H-12
6		142.9	H-2, H-7, H-8	14	2.55	30.0	
7	3.43	42.1	H-8, H-12, H-13	15	2.34	21.6	H-3, H-5
8	2.62	39.0	H-7, H-11				
	2.88						

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